A NEW FLUORESCENCE SPECTRUM OF URANYL AMMONIO-CHLORIDE.

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

THE spectrum of a sample of uranyl chloride (from Kahlbaum) when excited to fluorescence at the temperature of the room was measured by the present writers in 1911.[1] Like the fluorescence spectra of other uranyl salts it was found to consist of a series of nearly equidistant bands extending from the red to the blue. The crests of the six brightest bands, according to our observations, were at .5928μ, .5631μ, .5369μ, .5121μ, .4950μ, and .4769μ. At low temperatures this spectrum, which is comparatively feeble at + 20°, is resolved into a complex of very narrow bands similar to those described,[2] in the case of the other uranyl salts, by J. Becquerel and Onnes.

In the preparation of uranyl compounds, undertaken for us in the chemical laboratory of Cornell University by Mr. G. O. Cragwell a uranyl salt was obtained in the form of tri-clinic crystalline plates which we have since found to have the composition $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$.

These crystals are strongly fluorescent, and the fluorescence spectrum, unlike that of the other uranyl salts thus far described, is resolved at room temperature into at least eight groups of narrow bands. Each group, which corresponds to a single band of the ordinary uranyl fluorescence spectrum, consists of five nearly equidistant bands.

The symmetry of this spectrum, as it appears to the eye when viewed with a spectroscope of moderate dispersion, is most striking. While not so narrow as some of the line-like bands of uranyl spectra when excited at the temperature of liquid air, the bands are well separated from their neighbors and are about 18 Ångström units in width or one tenth as wide as the bands of the ordinary type of the uranyl fluorescence spectrum at + 20° C. Each group of five, indeed, occupies approximately the same space in the spectrum as an ordinary single band.

The distribution of intensities within the group was determined for the visually brightest group (.5302 ··· .5114), by means of the spectro-

[1] Nichols and Merritt, PHYS. REV. (1), XXXIII., p. 355.

[2] J. Becquerel and Onnes, Leiden Communications, 110, 1909.

photometer. The results are given in Table I. and are shown graphically in Fig. 1.

TABLE I.

Intensities of Bands in Group 6. (*Excited at* + 20°.)

Band.	Intensity.
.5302μ	18
.5253	33
.5203	24
.5157	11
.5114	[1]

[1] Visible but too dim for spectrophotometric measurement.

The curve (Fig. 1) which forms an envelope of the group of bands is of the same type as that for the distribution of intensities in a single band of the ordinary uranyl fluorescence spectrum and of the envelope of the set of bands in such a spectrum and is also similar to curves of distribution of the fluorescent spectra having a single broad band, such as resorufin.[1]

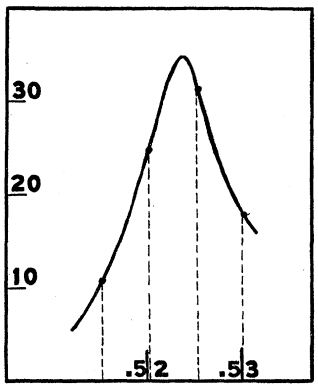

Fig. 1.

The effect of cooling is likewise analogous, the envelope for − 185° being narrower on account of the great relative reduction in brightness of the outlying members of the group. All the bands are shifted in position as well as changed in intensity in a manner to be described in a subsequent paragraph.

To determine as closely as possible the wave-lengths of the bands, photographs of the spectrum were taken. Fluorescence was excited by means of the carbon arc, the light from which passed through a screen opaque to rays of wave-length greater than about .45μ and was focused upon the crystal. Various exposures were employed on account of the great differences in the intensity of the bands and special plates were used for the red end of the spectrum. The exciting light was excluded from the camera by the use of suitable screens opaque to the blue and violet except where the absorption spectrum was to be recorded.

The various negatives were measured by mounting them on a micrometer stage in the field of the lantern. The micrometer screw was carefully calibrated so that wave-lengths could be determined by measuring the distance of the crests of the bands from certain reference lines of the mercury spectrum which was photographed on each negative so as to overlap the fluorescence spectrum.

[1] Nichols and Merritt, *l. c.*

This method of projection was found better than the use of the comparator commonly employed in the measurement of line spectra, because of the hazy character of the bands and because bands that are so weak and vague as to be invisible even under a low power microscope could be seen and located by means of the lantern. Many measurements of the stronger bands were made with comparator as a check on the determinations with the lantern.

The results of these measurements confirmed to a remarkable degree the apparent symmetry of the spectrum. When all the bands are plotted on a large scale, in a diagram with the reciprocal of wave-lengths as abscissae, the spectrum is seen to consist of eight groups of five bands each as already described. The bands of each group are very nearly equidistant, and corresponding members of the groups form an homologous series of equidistant bands. This interval moreover is very nearly the same for all five of these homologous series; but although the departures from equality are of the same order as the errors of measure-

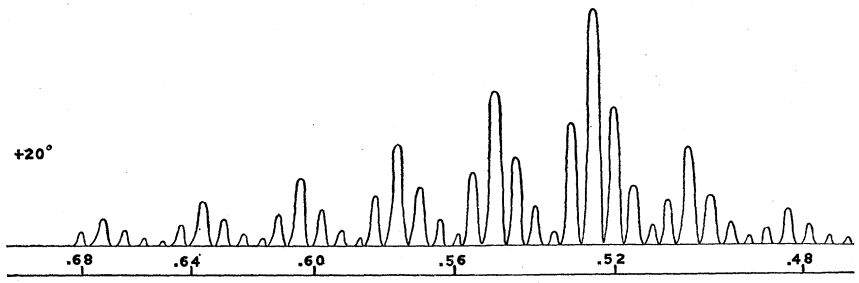

Fig. 2.

ment there is strong reason to regard them as real. Finally the groups taken as units and counting from their centers (obtained by averaging the frequencies of the bands in each) are equally distant within the errors of measurement.

The location of the various bands, as determined from the photographs, are given in Table II. The positions of the bands and their relative intensity, as estimated by the eye, are shown in Fig. 2. Horizontal distances are plotted on the scale of frequencies, the corresponding wave-lengths being indicated for convenience. In group 1, which lies in the red, band *e* is missing while in group 8 only the strongest band (*c*) was visible in any of the photographs.

This spectrum approximates very closely, *i. e.*, in most cases within or almost within the errors of observation, to a series of equidistant groups each consisting of five equidistant bands; distance being expressed in frequency. Were this strictly true the frequency interval of the

TABLE II.

Observed Positions of Bands at + 20°.

Group.	Band.	λ	1/λ×10³	Group.	Band.	λ	1/λ×10³
	b	.6804	1,469.7		*b*	.5547	1,802.8
	c	.6711	1,489.9		*c*	.5493	1,820.5
1	*d*	.6635	1,507.1	5	*d*	.5437	1,839.4
	e	.6585	1,521.8[1]		*e*	.5387	1,856.0
	a	.6501	1,538.2		*a*	.5344	1,871.2
	b	.6438	1,553.3		*b*	.5302	1,886.1
	c	.6356	1,573.4		*c*	.5252	1,904.0
2	*d*	.6293	1,588.9	6	*d*	.5201	1,922.6
	e	.6230	1,605.1		*e*	.5157	1,939.2
	a	.6167	1,621.5		*a*	.5114	1,955.3
	b	.6101	1,638.9		*b*	.5076	1,970.1
	c	.6039	1,655.9		*c*	.5035	1,986.2
3	*d*	.5978	1,672.8	7	*d*	.4986	2,005.7
	e	.5919	1,889.4		*e*	.4944	2,022.6
	a	.5862	1,705.9		*a*	.4906	2,038.3
	b	.5814	1,719.9		*b*	.4870	2,053.3[1]
	c	.5751	1,738.7		*c*	.4828	2,071.0
4	*d*	.5697	1,755.4	8	*d*	.4787	2,089.0[1]
	e	.5643	1,772.2		*e*	.4749	2,105.9[1]
	a	.5589	1,789.1		*a*	.4714	2,121.5[1]

homologous series of bands, *b*, *c*, *d*, *e* and *a* would be the same, and for each uniform throughout the spectrum and this interval would be the same as that between the successive groups taken as a whole. Finally the distances between neighboring bands would be the same within each group and for each group.

To test the intervals between groups the position of what may be called the center of each group was found by averaging the frequencies of all five bands and the intervals between these average positions for groups 2, 3, 4, 5, 6 and 7 were found.

Groups 1 and 8, for which insufficient data were available, were omitted.

The results are given in the tables III and IV.

The departures from uniformity in the intervals between groups (Table III.) are of the same order as the errors of observation and there is no indication of a progressive or systematic change. We may conclude therefore that within the accuracy of these measurements, *the groups are equidistant.*

[1] Band *e* (group 1) and bands *b*, *d*, *e* and *a* (group 8), which were indistinguishable in the photographs, have been assigned positions on the assumption of complete symmetry throughout the spectrum.

TABLE III.

Distance Between Groups.		
Group.	Center.	Intervals.
2	1,588.8	
3	1,671.7	82.96
4	1,754.6	82.86
5	1,837.8	83.20
6	1,921.2	83.40
7	2,003.9	82.76

TABLE IV.

Distance Between Neighboring Bands (Average).		
Band.	Center of Series.	Intervals.
b	1,762.1	
c	1,779.9	17.86
d	1,797.6	17.73
e	1,814.1	16.49
a	1,830.1	16.01

In a similar manner averages were found for the frequencies of each of the sets of homologous bands (*b*, *c*, *d*, *e*, *a*), and these form a group of averages, not coinciding with any actual group in the spectrum, the distances between the bands of which should however represent the mean distances of neighboring bands more closely than do the actual distances in any single group taken separately.

These averages are given in Table IV. from which it appears that the bands are not distributed uniformly within the group but that the distance between them *diminishes progressively as we pass towards the violet.* The distance between the last band (*a*) of any group and the first (*b*) of the next group is so nearly equal to the distances between the bands within the group that it was difficult, before the completion of these computations, to decide as to the boundaries between the groups. The casual appearance of the spectrum as may be seen from Fig. 2 is that of a succession of equidistant bands varying periodically in intensity. It was at first thought that the crest band (*c*) of each group formed the center with two weaker bands on either side and band (*a*) was supposed to be the first in each group counting from red towards violet. This designation has not been altered although it was found by measurement that band *a* in each group was distinctly nearer to band *b* (average distance 14.4) than to band *e* and should be considered as the last band of the group.

THE DETAILED STUDY OF THE INTERVALS OF THE SEVERAL HOMOLOGOUS SERIES OF BANDS (*b*, *c*, *d*, *e*, *a*).

To compare the intervals between homologous bands these were averaged for each series separately by the method of subtracting the frequency of each band of the series from the member of greater frequency and dividing the sum by the total number of intervals. The averages thus computed are as follows:

TABLE V.

Average Intervals between Homologous Bands.

Series.	Interval.
b (7 members)	83.19
c (8 members)	82.80
d (7 members)	83.25
e (6 members)	83.42
a (7 members)	83.26
General average,	83.20

For homologous series *b*, *d*, *e* and *a* the average distance between bands is the same within the errors of observation and approximately equal to the distance between the various groups considered as units. The interval for series *c* is smaller than for the other series and the difference, while scarcely larger than might be accounted for by experimental errors, appears to be a real one, appearing consistently in all the photographs taken of this spectrum and likewise in the case of spectrophotometric observations made to check the photographic determinations. To ascertain whether the groups of bands as individually measured really conformed to the description suggested in an earlier paragraph of a system of equidistant groups consisting of five homologous series of equidistant bands having a common interval, the positions of the members of a hypothetical system of this sort were computed in the following manner and the individual departures of the actual bands were determined.

It was assumed that the measurements of series *c* were slightly at fault and that the proper interval for the entire system was the average for the other four series, *i. e.*, 83.25. Using this interval the hypothetical bands were located about the "center" of each series and their positions were compared with those of the corresponding actual bands.

The results are shown in the following table in which the frequencies of the hypothetical bands are given in the columns marked "calculated," those of the actual bands in the columns marked "observed" and departures in those marked "differences."

THE EFFECT OF TEMPERATURE.

Ordinarily, when a uranyl salt is cooled to the temperature of liquid air the series of equidistant bands of its fluorescence spectrum, each of which corresponds to one of the eight groups of five narrower bands already described in the case of this form of uranyl ammonio-chloride, is resolved into a rather complex aggregation of narrow line-like bands.[1]

[1] See H. Becquerel, Comptes Rendus, 144, p. 671; also J. Becquerel and Onnes, Leiden Communications, No. 110, 1909.

TABLE VI.

Calculated and Observed Frequencies of the Various Series of Bands.

Series.	Group.	Calculated.	Observed.	Differences.	Intervals.
	1	1,470.3	1,469.8	+ .5	
	2	1,553.6	1,553.3	+ .3	83.60
	3	1,636.8	1,638.9	−2.1	85.60
b	4	1,720.1	1,719.9	+ .2	81.00
	5	1,803.3	1,802.8	+ .5	82.95
	6	1,886.6	1,886.1	+ .5	83.30
	7	1,969.8	1,970.1	− .3	83.95
	8	2,053.1			
	1	1,488.6	1,489.9	−1.3	
	2	1,571.8	1,573.4	−1.6	83.55
	3	1,655.1	1,655.9	− .8	82.45
c	4	1,738.3	1,738.7	− .4	82.85
	5	1,821.5	1,820.5	+1.0	81.80
	6	1,904.7	1,904.0	+ .7	83.50
	7	1,988.0	1,986.2	+1.8	82.25
	8	2,071.2	2,071.0	+ .2	84.85
	1	1,506.2	1,507.1	− .9	
	2	1,589.5	1,588.9	+ .6	81.80
	3	1,672.7	1,672.8	− .1	83.90
d	4	1,756.0	1,755.4	+ .6	82.65
	5	1,839.2	1,839.4	− .2	84.00
	6	1,922.5	1,922.6	− .1	83.15
	7	2,005.7	2,005.7	0	83.15
	8	2,089.0			
	1	1,522.7			
	2	1,605.9	1,605.1	+ .8	
	3	1,689.2	1,689.4	− .2	84.10
e	4	1,772.4	1,772.2	+ .2	82.85
	5	1,855.7	1,856.0	− .3	83.75
	6	1,938.9	1,939.2	− .3	83.20
	7	2,022.2	2,022.6	− .4	83.45
	8	2,105.4			
	1	1,538.7	1,538.2	+ .5	
	2	1,622.0	1,621.5	+ .5	83.25
	3	1,705.2	1,705.9	− .7	84.40
a	4	1,788.5	1,789.1	− .6	83.20
	5	1,871.7	1,871.2	+ .5	82.20
	6	1,955.0	1,955.3	− .3	84.10
	7	2,038.2	2,038.3	− .1	83.00
	8	2,121.4			

It was deemed of interest to determine the effect of temperature on a spectrum which was already at least partially resolved at + 20° and for

this purpose the ammonio-chloride under consideration in the present paper was subjected to cooling. Visual measurements of such of the bands as could be determined in this way were made at + 20°, 0°, − 30°, − 60°, − 90°, − 120°, − 150° and − 180°. Several sets of photographs of the spectrum were likewise obtained with the substance excited at − 185°.

When the substance, excited to fluorescence in the manner already described, was gradually cooled to the temperature of liquid air and as the spectrum was observed through the Hilger spectrometer the following changes were noted:

1. The bands become narrower and better defined until at the temperature of liquid air they correspond in appearance to the usual line like bands characteristic of the fluorescence spectra of the uranyl salts at low temperatures.

2. There is a shift towards the violet *amounting to more than a third of the distance between the bands.*

3. The following new bands appear: At about − 25° a very narrow band between *c* and *d* of each group; feeble at first but increasing in brightness with falling temperature. At about − 90° the *c* bands begin to appear double or in other words a new set becomes visible between *c* and *b*. At about − 150° another set of bands becomes visible between *e* and *a*.

Were the shift noted above the same for the different bands in each group and throughout all the groups, the spectrum at − 185°, at least as to the series, *b*, *c*, *d* and *e*, which are visible at both temperatures, would be located throughout by applying the mean observed shift to all the bands of the spectrum at + 20°.

The nature of the shift which these bands undergo appears to be as follows:

Each band may be regarded as an unresolved doublet, of which in general the member of longer wave-length is relatively so much the stronger that its position determines approximately the location of the crest of the composite band (see Fig. 3). The effect of cooling is to resolve this doublet into separately distinguishable bands and at the same time to cause a subsidence of the stronger and an increase of the weaker member. The member of shorter wave-length becomes dominant at low temperatures in each doublet and the arrangement of the entire spectrum therefore appears to be undisturbed but shifted towards the violet by an amount representing the width of the doublet.

Since however the doublet is now resolved by the narrowing of the components we might expect to be able to distinguish the original member

of longer wave-length unless by cooling it has disappeared altogether. The appearance of the group, if this be its real structure (*i. e.*, a set of equidistant doublets, the distance between the members of all the doublets being nearly the same) would then be as shown in the lower part of Fig. 3 ($-$ 185°).

At + 20° b', c', d', e' and a' are entirely concealed by the overlapping

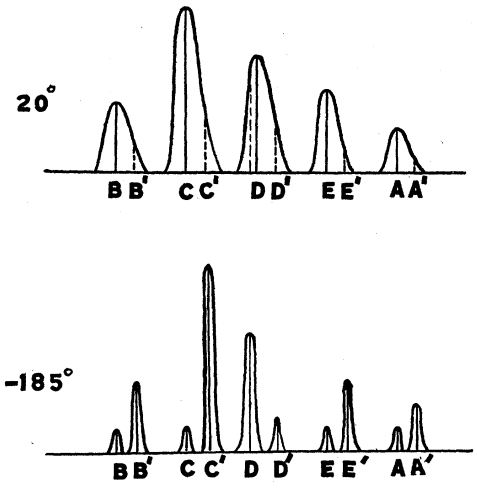

Fig. 3.

of the bands. At $-$ 185° b, c, d, e and a may or may not be visible according to their intensity or to the completeness of the resolution which in fact differs greatly in different portions of the spectrum. At $-$ 185° however b, c, d, e and a being very weak as compared with b', c', d', e' and a' or in some cases almost invisible, the appearance is that of a shift equal to the distance bb', cc', etc.

TABLE VII.

Shift of the c Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+ 20°.	−185°.	Shift.
	1	1,489.9	1,496.5	6.6
	2	1,573.4	1,579.8	6.4
	3	1,655.9	1,662.1	6.2
c	4	1,738.7	1,744.4	5.7
	5	1,820.5	1,827.7	7.2
	6	1,904.0	1,910.6	6.6
	7	1,986.2	1,992.7	6.5
	8	2,071.6	———	——
			Average,	6.5

When we apply this test, making use of the photographic measurements at − 185°, we find for series *c* a shift that is uniform throughout the spectrum, see Table VII.

It follows, obviously, that the interval for the *c* series is the same, within the errors of observation, at − 185° and at + 20°. The actual averages from observed positions are respectively: 82.8 (+ 20°) and 82.5 (− 185°).

For the *b* series we obtain likewise a constant shift except in the extreme red (groups 1 and 2) where the bands are so faint as to be almost indistinguishable and the resolution is imperfect so that the vague bands on the negatives are probably composite (see Table VIII.).

TABLE VIII.

Shift of the b Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+20°.	−185°.	Shift.
	1	1,469.7	1,479.7(?)	10.0(?)
	2	1,553.3	1,563.0(?)	9.7(?)
	3	1,638.9	1,645.0	6.1
b	4	1,719.9	1,726.9	7.0
	5	1,802.8	1,810.4	7.6
	6	1,886.1	1,894.4	8.3
	7	1,970.1	1,977.9	7.8
	8	———	———	——
		Average (omitting groups 1 and 2), 7.7		

In the case of the *d* series the effect of the lack of resolution in the red end of the spectrum is more clearly marked and is capable of definite description. Here we find the bands of groups 4, 5, 6 and 7 in their expected places and showing the proper shift (see Table IX.), whereas

TABLE IX.

Shift of the d Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+20°.	−185°.	Shift.
	1	1,507.1	1,508.9	1.8
	2	1,588.9	1,591.5	2.6
	3	1,672.8	1,675.6	2.8
d	4	1,755.4	1,761.4	6.0
	5	1,839.4	1,845.1	5.7
	6	1,922.6	1,929.2	6.6
	7	2,005.7	2,013.4	7.7
	8	———	2,097.1	——
			Average (groups 4 to 8), 6.5	

Average interval at +20° = 83.24

Average interval (groups 4 to 8) at −185° = 83.93

in groups 1, 2 and 3 they are considerably displaced towards the violet having a position intermediate between the places which the band *d* and the new intermediate bands should occupy. In other words in these groups of longer wave-length, these bands, which in the remainder of the spectrum are separate and well defined, are not resolved.

The interpretation of the changes occurring in the regions of the spectrum occupied by the *d*, *e* and *a* bands is most readily studied by means of the diagram in Fig. 4, in which the bands of each group at

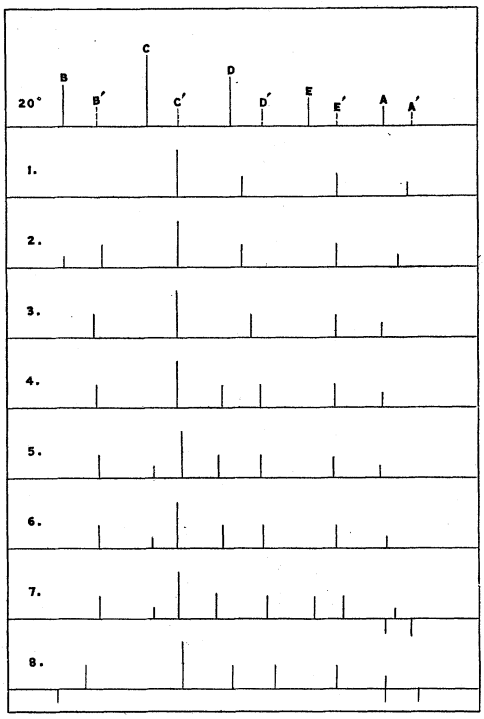

Fig. 4.

− 185° are shown in their relation to a hypothetical grouping given at the head of the column. This grouping consists of the set of imagined doublets of which as in a previous paragraph the spectrum at + 20° was supposed to be made up. The spacing for each doublet is that determined from the observed shift on cooling and the relative divergence from this arrangement is shown for all the bands of each group.

A scrutiny of the fluorescence spectrum at − 185° group by group, by means of this diagram, affords very satisfactory confirmation of this hypothesis concerning the apparent shift. It is obvious:

1. That not all the components *b*, *c*, *d*, *e* and *a* will necessarily be visible in every group of the resolved spectrum:

2. That lack of resolution in any region may give the appearance of a single band with intermediate crest in place of the doublet:

3. That the position of crests of the unresolved doublets at + 20° will not necessarily coincide exactly with that of either component.

Bearing these points in mind, it will be seen that were resolution complete all the oserved bands of the spectrum at − 185° would probably fall into the system proposed above.

We may imagine that the difference between the resolution of the bands *c* and *d*, for example as seen in Fig. 4, is produced by changes in the unresolved doublets at + 20° when the temperature is reduced to − 185°, of the kind indicated in Fig. 5. The doublet *cc'* forms a single band with crest nearly coincident with *c* at + 20° and this owing to the

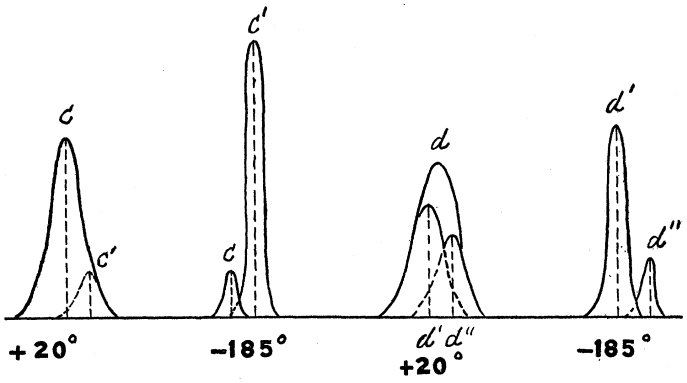

Fig. 5.

subsidence of *c* and growth of *c'* takes the resolved form shown at − 185°. In the case of *d* however the unresolved band has an intermediate crest at *d* but is really composed of overlapping components *d'* and *d''* which are separately visible at − 185°.

THE ABSORPTION SPECTRUM.

The absorption spectrum of this salt of which observations were made both visually and photographically likewise consists of several series of equidistant bands having a common interval.

Fluorescence and absorption overlap as in the case with all the uranyl spectra thus far studied, and one group of bands (group 7 of the fluorescence spectrum) which we have called the *reversing group* is common to both spectra. The bands of this group may be made to appear either as fluorescence bands or as absorption bands according to the conditions of the experiment. The reversal may be effected by the simple expedient of varying the character of the incident light. With a screen which

extinguishes the yellow and green and transmits shorter wave-lengths the fluorescence bands of this region appear on a dark background. With a yellow screen that reduces excitation to a minimum, absorption bands are seen to take their place. These, in general, coincide in position with the fluorescence they displace, but since as has been shown the bands are doublets of unequal brightness an apparent shift sometimes occurs.

The weaker band of the fluorescence pair becomes the stronger in the absorption spectrum as illustrated in Fig. 6, which is from a photograph

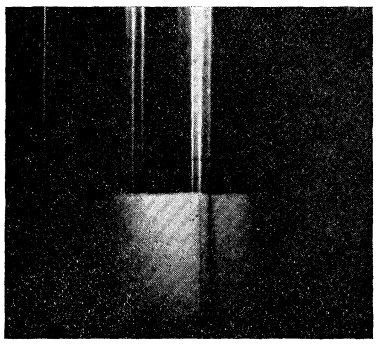

Fig. 6.

of such a doublet when emitting and when absorbing light. In such cases the weaker bands are often invisible unless special precautions are taken to bring them out and there is an apparent shift equal to the distance between the members of the doublet.

Since the temperature shift in the bands of the fluorescence spectrum, as stated in a previous paragraph, is mainly due to the subsidence of the stronger and the "crudescence" of the weaker member of such doublets, upon cooling to the temperature of liquid air we should expect the location of the absorption bands when thus displaced at room temperature to coincide with the low temperature positions of fluorescence, and this is found to be the case in many instances.

Unfortunately the complete analysis of the absorption spectrum is rendered difficult, not only by the varying degrees of resolution, as in the case of the fluorescence bands, but also by the existence of a general absorption which increases rapidly towards the violet and renders the crystals almost opaque to the violet and ultraviolet rays.

The absorption spectrum at $+ 20°$ extends from the reversing region into the ultraviolet.

It consists of the following series:

1. $\beta\alpha$; so designated because its first member at $.5076\mu$ ($1/\lambda \times 10^3$

= 1,970) is coincident with and a reversal of the b band in that group, while its second member at .4899μ ($1/\lambda \times 10^3 = 2{,}041$) is so nearly coincident with the a band of the same group that it may be supposed to form a close and unresolved doublet with the absorption series related to that band.

2. γ; having its first member at .5028μ ($1/\lambda \times 10^3 = 1{,}989$) and the reversal of the c band in that group.

3. δ' and δ; two series, having their origin on either side of the d band; as if this band were a doublet, unresolved in the fluorescence but resolved in portions of the absorption spectrum.

4. ϵ and ϵ'; two series, one of which ϵ begins as the reversal of the e band at .4942 ($1/\lambda \times 10^3 = 2{,}023$) while the companion series ϵ', which possibly belongs to an unresolved component of the e band, first becomes distinguishable as a faint absorption band at 2,173.

The constant frequency interval common to all these series is approximately 71[1] instead of 83.2 which is the average interval for the fluorescence bands. This sudden break to a shorter interval in passing from fluorescence to absorption is not new. It is characteristic of all absorption spectra of the uranyl salts thus far studied at room temperature[1] and corresponds, approximately, with the intervals between the absorption bands of solutions of these salts given by Jones and Strong.[2] We have tried in vain not only in the case of the chloride but likewise with the

[1] See Nichols and Merritt, PHYS. REV., Vol. 33, p. 354.

TABLE X.

Relation Between Absorption bands of UO_2Cl_2 *in Solution (.49μ to .67μ) and the α, γ, δ and ϵ Series.*

UO_2Cl_2 in H_2O Jones and Strong.		Corresponding Series of $2NH_4Cl.UO_2Cl_2+2H_2O$ (Crystals).	
λ	$1/\lambda \times 10^3$	Series.	$1/\lambda \times 10^3$ (Computed).
.6700	1,492	γ	1,492
.6500	1,538	α	1,544
.6300	1,587	δ	1,583
.6070	1,647	δ'	1,646
.6040	1,656	δ	1,653
.6020	1,661	–	——
.6000	1,667	ϵ	1,668
.5480	1,825	α	1,828
.5200	1,923	–	——
.5185	1,929	δ'	1,930
.4900	2,041	α	2,041

[1] The actual observed range, as will be seen from Table XI., is from 70.4 for series γ to 71.5 for series $\beta\alpha$, and these differences are presumably due to the varying relations of the unresolved components of the doublets of which the bands are composed.

[2] Jones and Strong, Publications of the Carnegie Institution, No. 130, p. 89, also Physikalische Zeitschrift, 10, p. 497.

crystals of the nitrate and with other solid uranyl salts, to trace the absorption into the realm of the fluorescence spectrum. Jones and Strong, however, working with solutions of uranyl chloride in water, have located various absorption bands of longer wave-lengths.

TABLE XI.

"Absorption" Bands of $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ *at* + 20° *C. Arranged in Series.*

Series $\beta\alpha$.			Series γ.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
5,076	1,970.1		5,029	1,988.5	
4,899	2,041.2		4,860	2,057.5	
4,733	2,113.0		4,704	2,126.0	
4,577	2,185.0		——	——	
4,433	2,256.2		——	——	
4,293	2,329.5	71.5	——	——	70.4
4,166	2,400.3		——	——	
——	——		——	——	
——	——		——	——	
——	——[1]		3,815	2,620.9	
——	——[1]		3,714	2,692.8	
3,627	2 756.8		——	——	
Series δ'.			Series δ.		
4,996	2,001.6		4,978	2,008.9	
4,829	2,070.6		4,908	2,080.1	
4,667	2,142.6		4,652	2,149.5	
——	——		4,507	2,218.9	
——	——		4,370	2,288.5	
——	——	70.7	4,237	2,359.9	70.5
——	——		4,112	2,432.0	
——	——		3,997	2,501.8	
3,898	2,565.1		3,885	2,573.7	
3,792	2,637.1		——	——	
3,692	2,708.6		3,685	2,713.7	
Series ϵ.			Series ϵ'.		
4,942	2,023.3		——	——	
4,776	2,094.0		——	——	
4,618	2,165.5		4,601	2,173.5	
——	——		4,455	2,244.5	
4,331	2,309.0		4,320	2,314.6	
4,202	2,379.9	70.9	4,194	2,384.6	71.0
——	——		4,073	2,455.2	
——	——		3,957	2,527.4	
3,863	2,588.7		——	——	
3,757	2,661.7		——	——	
——	——		3,648	2,741.2	

[1] Two bands at 2,604.6 and 2,675.2 are perhaps to be regarded as members of this series but displaced about 10 to the red. They are designated as α'.

We were surprised to find that of eleven bands indicated by them as lying between .4900μ and .6700μ nine might be considered as related to the various series described in the present paper. In the following table the wave-lengths and frequencies of these bands are given together with the frequency of the corresponding member of our series computed on the assumption of its extension towards the red with the constant interval of 71.

Considering that the bands of Jones and Strong are for the simple chloride in solution, it might be held that a comparison with bands of a double chloride in the crystalline form is entirely without significance. It has seemed worth while however to call attention to these approximate coincidences of position.

Table XI. gives the bands thus far located in the absorption spectrum at + 20° C. It will be noted that series γ and δ' disappear after the

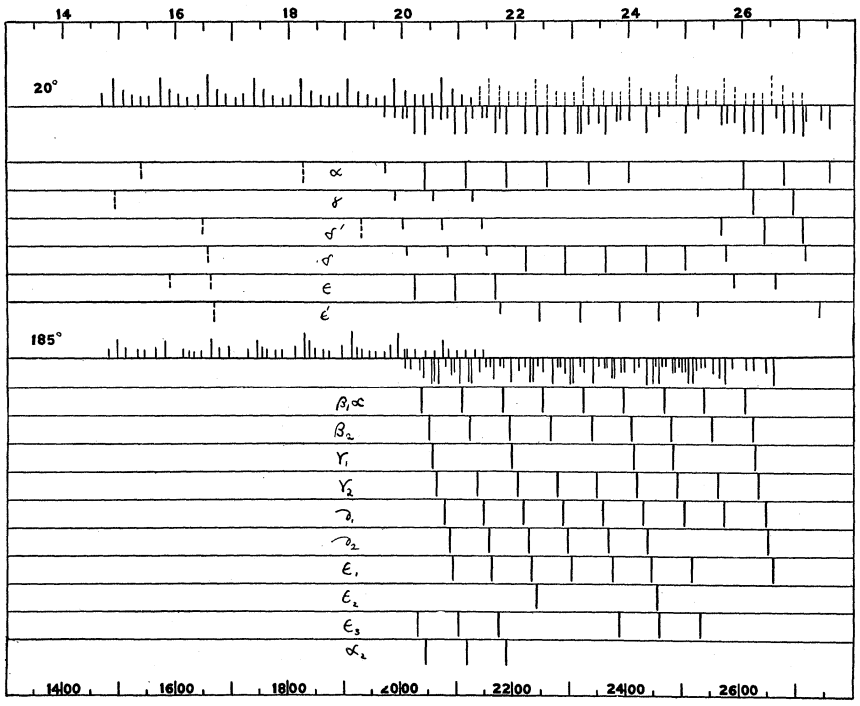

Fig. 7.

third member but reappear in the extreme violet; also that δ, which appears as a doublet with δ' at both ends of the spectrum, continues throughout the wide gap between .47μ and .39μ where γ and δ' are missing.

The absorption spectrum of this salt at $-185°$ undergoes changes strictly analogous to those described in the case of the fluorescence spectrum. There is the usual narrowing of the bands with further resolution. The bands in the absorption spectrum however are still capable of arrangement in series with a nearly constant frequency interval of about 71 and these series in general have their origin in coincidence with a fluorescence series. The apparent exceptions are undoubtedly due to the fact that the bands, both of fluorescence and absorption, are complex and only partially resolved.

The general grouping of the fluorescence and absorption bands at

TABLE XII.

"Fluorescence" Bands of $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ *at* $-185°$ *C. Arranged in Series.*

Series b_1.			Series b_2.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
——	——		6,758	1,479.7	
——	——		6,398	1,563.0	
6,110	1,636.7		6,079	1,645.0	
——	——	83.0	5,791	1,726.9	83.2
——	——		5,524	1,810.4	
——	——		5,279	1,894.4	
5,080	1,968.7		5,056	1,977.9	
Series c.			Series d_1.		
6,682	1,496.5		——	——	
6,330	1,579.8		——	——	
6,016	1,662.1		——	——	
5,733	1,744.4	82.6	5,704	1,753.1	83.8
5,471	1,827.7		5,445	1,836.7	
5,234	1,910.6		5,206	1,921.0	
5,018	1,992.7		4,989	2,004.5	
Series d_2.			Series e_1.		
6,628	1,508.9		——	——	
6,283	1,591.5		——	——	
5,968	1,675.6		——	——	
5,677	1,761.4	84.2	——	——	82.4
5,420	1,845.1		5,379	1,859.0	
5,184	1,929.2		5,149	1,941.9	
4,967	2,013.4		4,940	2,024.1	
Series e_2.			Series a.		
6,538	1,529.6		——	——	
6,207	1,611.0		——	——	
5,899	1,695.0	83.3	——	——	83.1
5,624	1,778.1		5,595	1,787.3	
5,370	1,862.0		5,345	1,870.8	
5,141	1,945.0		5,118	1,953.7	

TABLE XIII.

Absorption Bands of $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ *at* $-185°$ *C. Arranged in Series.*

Series $\beta_{1\alpha}$.			Series β_2.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
4,906	2,038.5		4,875	2,051.1	
4,742	2,109.0		4,711	2,122.7	
4,587	2,180.2		4,560	2,193.1	
4,443	2,250.9		4,413	2,265.9	
4,305	2,322.8	71.2	4,277	2,338.2	71.5
4,177	2,394.0		4,152	2,408.7	
4,054	2,466.8		4,034	2,479.0	
3,941	2,537.3		3,922	2,550.1	
3,833	2,609.0		3,813	2,622.7	
Series γ_1.			Series γ_2.		
4,863	2,056.5		4,843	2,064.7	
——	——		4,680	2,136.5	
4,551	2,197.3		4,530	2,207.3	
——	——		4,389	2,278.3	
——	——	71.5	4,259	2,348.1	71.1
4,146	2,411.9		4,134	2,419.0	
4,028	2,482.5		4,016	2,489.9	
——	——		3,904	2,561.6	
3,808	2,626.3		3,798	2,633.0	
Series δ_1.			Series δ_2.		
4,813	2,077.9		4,792	2,086.8	
4,654	2,148.9		4,639	2,155.5	
4,508	2,218.2		4,490	2,227.0	
4,370	2,288.5		4,352	2,298.0	
4,239	2,359.1	71.0	4,222	2,368.3	70.5
4,114	2,430.9		4,102	2,437.9	
3,997	2,502.0		——	——	
3,886	2,573.2		——	——	
3,780	2,645.5		3,774	2,650.0	
Series ϵ_1.			Series ϵ_2.		
4,778	2,092.7		——	——	
4,625	2,162.1		——	——	
4,478	2,233.0		4,460	2,242.2	
4,341	2,303.4		——	——	
4,209	2,376.0	70.7	——	——	70.9
4,090	2,445.0		4,073	2,454.9	
3,975	2,515.8		——	——	
——	——		——	——	
3,763	2,657.5		——	——	

TABLE XIII.—*Continued.*

Series ϵ_3.			Series a_2.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
4,924	2,031.0		4,889	2,045.5	
4,756	2,102.4		4,724	2,116.9	
4,599	2,174.4		4,571	2,187.7	
——	——		——	——	
——	——	71.4	——	——	71.0
4,188	2,387.5		——	——	
4,066	2,459.7		——	——	
3,951	2,530.7		——	——	
——	——		——	——	

+ 20° and − 185° is shown in Fig. 7 and the bands, arranged by series as determined from the observations at − 185° are given in Tables XII. and XIII. The different series in the absorption spectrum also shown graphically in Fig. 7. The dotted lines in the upper portion of this figure show the positions in which we should expect fluorescence bands to be found if the fluorescence had extended into the violet.

In a recent paper[1] it has been shown that the fluorescence and absorption of these crystals consists throughout of doublets polarized at right angles to each other and unresolved when the spectrum is observed without the aid of a Nicol prism or other analyzer. These polarized spectra and their relation to those described here will be considered in detail in a forthcoming article.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
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[1] Nichols and Howes, Proceedings of the National Academy of Sciences, Vol. 1, p. 444.

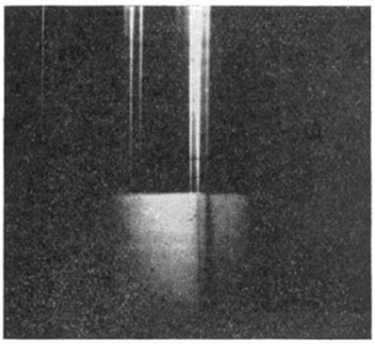

Fig. 6.